Quantum size effects in Pb layers with absorbed Kondo adatoms: Determination of the exchange coupling constant

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We consider the magnetic interaction of manganese phtalocyanine (MnPc) absorbed on Pb layers which were grown on a Si substrate. We perform an ab-initio calculation of the density of states and Kondo temperature as function of the number of Pb monolayers. Comparison to experimental data [Phys. Rev. Lett. 99, 256601 (2007)] then allows us to determine the exchange coupling constant J between the spins of the adsorbed molecules and those of the Pb host. This approach gives rise to a general and reliable method for obtaining J, by combining experimental and numerical results.

Strong correlation phenomena built the fundament of a number of extraordinary effects observed in condensed matter systems. One of the most drastic manifestations is the Kondo effect[1] arising from strong coupling between single localized spins and the conduction electrons. For an antiferromagnetic-type interaction below the characteristic Kondo temperature, T_K, this coupling cannot be treated perturbatively. It comes along with the formation of a narrow peak in the density of states (DOS) of a Kondo adatom pinned to the Fermi energy of the conduction electrons, ε_F. Its lineshape can be described by the well-known Doniach-Sunjic formula[2,3].

The appearance of the Kondo resonance has various physical consequences. In the context of the transport properties of bulk diluted magnetic alloys it manifests as enhancement of the resistance at low temperatures. In mesoscopic systems consisting of a single quantum dot coupled to a pair of one-dimensional leads[5,6] it results in a drastic enhancement of the conductance below T_K[7,8].

A system which recently has attracted much attention, both from the experimental and theoretical side, is composed of a metallic host surface with a Kondo adatom (adsorbed atom) and a STM tip, non- or ferromagnetic[9]. Contrasting the case of a single quantum dot coupled to leads, such a system demonstrates a much greater variety of transport regimes. This arises from the possibility of quantum interference between distinct transport paths, namely direct tip-host tunneling and indirect tip-adatom-host tunneling[10]. In particular, the latter process gets extremely efficient for temperatures below T_K due to the appearance of a Kondo resonance in the adatom spectral function. The quantum interference mechanism leads to an asymmetry of the Kondo resonance. Instead of a Lorentzian lineshape it acquires a Fano-type lineshape, which is characteristic of interference between a discret level and a continuous spectrum. The appearence of this kind of a Fano-Kondo resonance has been found in various experiments with nonmagnetic tips[10,11,12,13] and has been discussed in a number of theoretical works[15,16,17].

In a recent experimental work the quantum size effect on the Kondo temperature was investigated by Y.-S. Fu et al.[14]. The system under study consisted of individual manganese phtalocyanine (MnPc) molecules absorbed on ultrathin Pb films grown on Si(111). Scanning tunneling spectroscopy shows asymmetric Fano-Kondo peaks in the differential conductance. One central implication of the work by Y.-S. Fu et al.[14] is that the variation of the film thickness, given by the number of Pb monolayers (MLs), leads to drastic changes in T_K, more specifically to pronounced oscillations with a period of 2 MLs. The lowest (23 K) and highest (419 K) values occured at thicknesses of 15 and 17 MLs, respectively. Because the Kondo temperature scales with the electronic DOS at the Fermi energy, $\rho = \mathrm{DOS}(\varepsilon_F)$, according to

$$T_K = A \cdot e^{-1/(J\cdot\rho)}, \tag{1}$$

where A is an amplitude and J is the exchange coupling constant, this observation has been attributed to oscillations in the Pb DOS with the film thickness. Indeed, for every 2 MLs increase of the thickness one empty quantization band moves down below the Fermi level and gets occupied[18].

In the following we present a state-of-the-art ab-initio investigation of the electronic structure of Pb films on a Si(111) surface. Determining $\rho = \mathrm{DOS}(\varepsilon_F)$ as a function of the film thickness and using Eq. 1 we can perform a fit to the experimental data given in Fig. 2 of Ref. 14. Besides the amplitude A, the exchange coupling constant J is the only fitting parameter and therefore can be obtained without any further assumption.

Our analysis is based on the augmented spherical wave approach, applying density functional theory within the local density approximation[19]. This method is particularly suitable for dealing with unit cells containing many atoms[20,21,22], which are needed to describe interfaces, since it utilizes a minimal atomic-like basis set. For the present system this basis set consists of Si $3s$, $3p$, $3d$ as well as Pb $6s$, $6p$, $5d$ states, and is complemented by orbitals of additional augmentation spheres. Brillouin zone integrations are performed using the linear tetrahedron method, where we checked the convergence of the calculation with respect the fineness of the k-mesh by means of a growing number of up to 231 k-points in the irreducible wedge of the supercell Brillouin zone.

Our Si(111)/Pb(111) supercells comprise a Si slab of about 25 Å thickness, an attached Pb slab ranging from 1 to 18 Pb MLs, and a vacuum slab on top. For generating the supercells we have started from the hexagonal representation of the fcc lattice, with the (111) direction along the hexagonal c_{hex} axis. For the Pb slab we use the experimental lattice constant $a_{\mathrm{Pb}} = 4.95$ Å. Moreover, for attaching the Si slab ($a_{\mathrm{Si}} = 5.43$ Å) to the Pb slab we have to artificially shrink the former and introduce a lattice strain. Although this lattice strain in the Si slab is substantial, no drawback on the Pb electronic structure is to be expected since there are no Si states in the vicin-

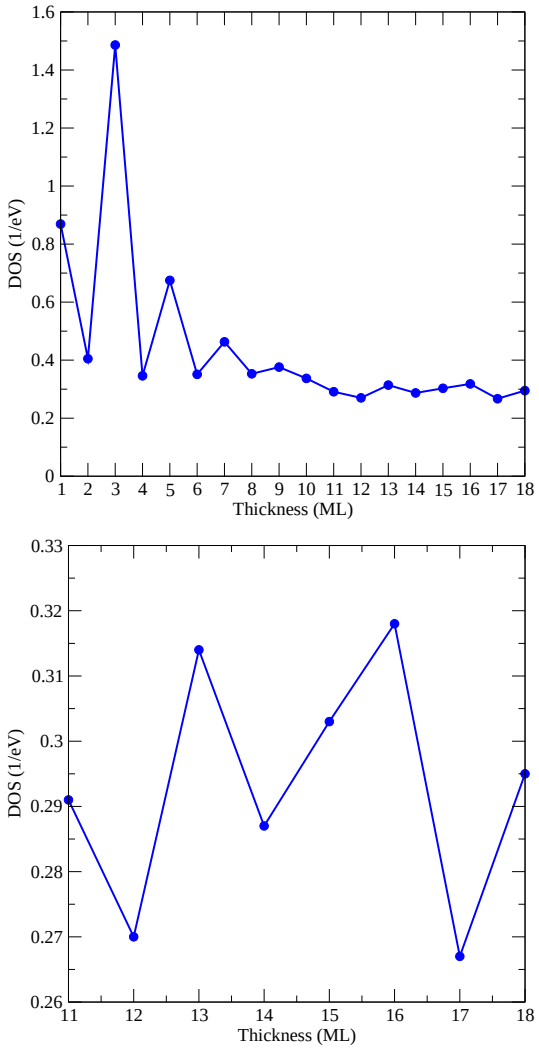

FIG. 1: Top: Total DOS at ε_F for a Pb(111) film on Si(111), depicted as a function of the number of Pb MLs. The values are normalized by the numbers of Pb atoms in the supercells. Bottom: Zoom for the 11-18 MLs range.

ity of the Fermi energy. Our supercells extend 121.25 Å along $c_{\rm hex}$ and have as basal plane a parallelogram with a 60° interior angle and edges of length $a_{\rm Pb}$.

We obtain for the DOS at the Fermi energy the results displayed in Fig. 1 as a funtion of the Pb film thickness. One clearly identifies the previously discussed oscillatory behavior, with a period of 2 MLs, up to a thickness of 9 MLs. Deviations from this regular scheme are found in the intervals 9-12 and 14-16 MLs where the oszillations are suppressed[23]. Comparing Fig. 1 to the experimental data[14] indicates that our curve is shifted by 1 ML to the left hand side, see particularly the position of the 14-16 MLs anomaly. This difference might either trace back to the experimental difficulty in counting the MLs or to the effects of the (planar) MnPc molecule on the local DOS, which is not included in our treatment. Since there is no ambiguity in the choice of the matching conditions at the Si–Pb interface, our approach elsewise should not lead to a 1 ML shift.

Using Eq. 1 we next calculate from our DOS data the dependence of the Kondo temperature on the film thickness. To that aim, we use the second highest (150 K at 12 MLs) and smallest (23 K at 15 MLs) of the experimentally observed T_K values to fit the free parameters A and J. The correctness of the highest measured temperature (419 K at 15 MLs) is quite dubious, see the discussion of the authors themselves, and thus not taken into consideration. At the Fermi energy, the ab-initio DOS amounts to 0.318 eV^{-1} for 12 MLs and to 0.267 eV^{-1} for 15 MLs. As a consequence, we obtain from Eq. 1 for the exchange coupling constant

$$J \approx 0.32 \pm 0.04 \text{ eV}.$$

As compared to semiconductor bulk systems[24], the value of J is 2–4 times smaller, which is not surprising because the coupling to a surface in general is much weaker than the coupling within the bulk.

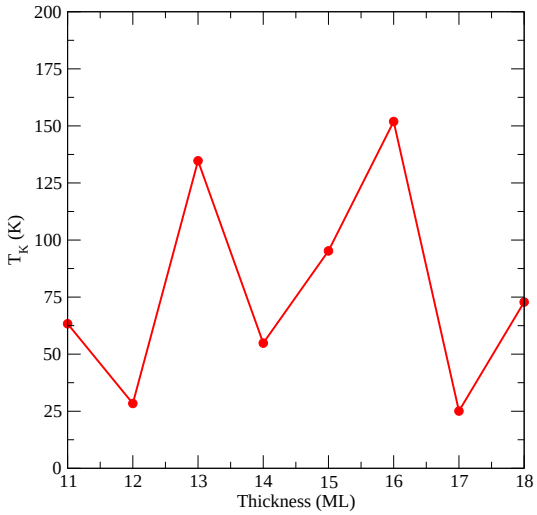

FIG. 2: Kondo temperature as a function of the thickness of the Pb(111) film, given by the number of Pb MLs.

Due to the logarithmic dependence on T_K, the determined value of J is particularly insensitive to experimental inaccuracies. The outcome of our fitting procedure is displayed in Fig. 2. As to be expected, the dependence of T_K on the film thickness largely resembles the behaviour of ρ, see the bottom of Fig. 1. We do not find indications of a dependence of the exchange coupling constant J on the film thickness between 11 and 18 MLs. Hence, there is a qualitative agreement with the experimental results, even though clarification of the 1 ML shift and T_K spike at 17 MLs should be tackled by future experiments.

In summary, we have performed first-principles calculations to establish the density of states of Pb(111) films grown on a Si(111) substrate. These ab-initio data have enabled us to fit experimental results from measurements addressing the dependence of the Kondo temperature on the Pb film thickness. In particular, we have succeeded in calculating the exchange coupling constant J, which is not accessible to direct experimental determination. For the system under investigation, a value of about $J = 1/3$ eV transpires.

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